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DESCRIPTION

POWER GENERATION CELL FOR SOLID ELECTROLYTE FUEL CELL

5 Cross-Reference to Prior Application

This is a U.S. National Phase Application under 35
U.S.C. §371 of International Patent Application No.
PCT/JP2004/016658, filed November 10, 2004, and claims the
benefit of Japanese Patent Application Nos. 2003-379477,
10 filed November 10, 2003 and 2003-379791, filed November 10,
2003, all of which are incorporated by reference herein.
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15

Technical Field

 The present invention relates to a power generation
cell for a solid electrolyte fuel cell, in which a lanthanum
gallate-based electrolyte is used as a solid electrolyte and,
20 more particularly, to an anode of a power generation cell
for a solid electrolyte fuel cell.

Background Art

 Generally, in a solid electrolyte fuel cell, hydrogen
gas, natural gas, methanol, coal gas or the like is used as
25 fuel, thus use of alternative energy for replacing petroleum

may be promoted in power generation. Furthermore, since it is possible to use waste heat, the solid electrolyte fuel cell is watched in views of resource nursing and the environment. The solid electrolyte fuel cell typically
5 includes a power generation cell having a structure in which a cathode is layered on a side of a solid electrolyte including oxides and an anode is layered on another side of the solid electrolyte. The solid electrolyte fuel cell also includes a cathode collector layered on an external side of
10 the cathode of the power generation cell, an anode collector layered on an external side of the anode of the power generation cell, and separators layered on the external sides of the cathode and the anode. The solid electrolyte fuel cell is typically operated at 800 to 1000°C. However,
15 recently, a low temperature-type solid electrolyte fuel cell, which is operated at 600 to 800°C, has been suggested.

It is known that a lanthanum gallate-based oxide ion conductor is used as a solid electrolyte constituting a power generation cell of the low temperature-type solid
20 electrolyte fuel cell, and that the lanthanum gallate-based oxide ion conductor is an oxide ion conductor expressed by the formula of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y-z}\text{Mg}_y\text{A}_z\text{O}_3$ (A is one or more of Co, Fe, Ni, and Cu, X is 0.05 to 0.3, Y is 0 to 0.29, Z is 0.01 to 0.3, and Y+Z is 0.025 to 0.3) (see JP-A-11-335164).

25 Additionally, it is known that the anode includes a

porous sintered body, which contains B-~~(B is one or more of Sm, Gd, Y, and Ca, and the same shall apply hereinafter)~~
doped ceria is expressed by the formula of $Ce_{1-m}B_mO_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$) and nickel.

5 Further, it is known that nickel of the porous sintered body including B-doped ceria and nickel forms a porous frame structure constituting a network, and that B-doped ceria has ~~the a~~ particle size of 0.1 to 2 μm and a network structure surrounding a surface of nickel of the porous frame
10 structure as shown in Fig. 3 (see JP-A-11-297333).

Furthermore, it is known that the anode includes the sintered body, which has B-doped ceria expressed by the formula of $Ce_{1-m}B_mO_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$) and nickel. The sintered body may have a
15 nickel composition gradient, thus a nickel content is increased in a thickness direction. Alternatively, the sintered body may include a plurality of layers having different nickel contents so that the nickel content is continuously or intermittently increased in the direction
20 from the innermost layer to the outermost layer.

~~Disclosure~~ Summary of the Invention

Since a current solid electrolyte fuel cell has a large size and has an insufficient output, there are demands for
25 size reduction and high output. There are also demands for

size reduction and high output of a solid electrolyte fuel cell, which has a conventional power generation cell including a sintered body containing B-doped ceria and nickel as an anode.

5 ~~Therefore, in the above mentioned point of view, the inventors of the invention have conducted research to develop a better solid electrolyte fuel cell. Thereby, the following results were obtained.~~

(a) In an anode having a structure where B-doped ceria
10 is attached to a surface of nickel of a porous frame structure in a particle form, when the amount of B-doped ceria particles, which are separately attached while the B-doped ceria particle is not in contact with the adjacent B-doped ceria particle, is large, characteristics of the solid
15 electrolyte fuel cell are improved. (b) As shown in Fig. 1, when the B-doped ceria particles, which are separately attached to the surface of nickel of the porous frame structure, include B-doped ceria particles, which are known in the art and have an average particle size of 0.2 to 0.6
20 μm (hereinafter, referred to as "large diameter ceria particle"), and B-doped ceria particles, which have an average particle size of 0.01 to 0.09 μm (hereinafter, referred to as "small diameter ceria particle") and are separately attached between the large diameter ceria
25 particles, it is possible to improve characteristics of the

solid electrolyte fuel cell.

(c) In the power generation cell for the solid electrolyte fuel cell in which a lanthanum gallate-based oxide ion conductor is used as a solid electrolyte, a porous cathode is formed on a side of the solid electrolyte, and a porous anode is formed on another side of the solid electrolyte, the anode includes a sintered body which contains B-doped ceria expressed by the formula of $\text{Ce}_{1-m}\text{B}_m\text{O}_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$) and nickel. In the sintered body, the B-doped ceria particles, which are expressed by the formula of $\text{Ce}_{1-m}\text{B}_m\text{O}_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$), are separately attached to the surface of nickel of the porous frame structure. Furthermore, the sintered body has a nickel composition gradient, thus a nickel content is increased in a thickness direction. The nickel content of the innermost surface of the anode which is in contact with the solid electrolyte is 0.1 to 20 vol%, and the nickel content of the outermost surface of the anode is 40 to 99 vol%. Thereby, it is possible to increase a power output.

(d) In the power generation cell for the solid electrolyte fuel cell in which the lanthanum gallate-based oxide ion conductor is used as the solid electrolyte, the porous cathode is formed on a side of the solid electrolyte, and the porous anode is formed on another side of the solid

electrolyte, the anode includes the sintered body which contains B-doped ceria expressed by the formula of $Ce_{1-m}B_mO_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$) and nickel. The sintered body includes a plurality of layers
5 having different nickel contents, in which B-doped ceria particles are separately attached to the surface of nickel of the porous frame structure. A plurality of layers includes at least the innermost layer, which has the nickel content of 0.1 to 20 vol% and is in contact with the solid
10 electrolyte, and the outermost layer, which has the nickel content of 40 to 99 vol% and is separated from the solid electrolyte at least by the innermost layer. Thereby, it is possible to increase a power output.

(e) An intermediate layer including a single layer or
15 two or more layers is formed between the innermost and the outermost layers having the different nickel contents disclosed in (d). The nickel content of the innermost layer is 0.1 to 20 vol%, and the nickel content of the outermost layer is 40 to 99 vol%. The intermediate layer including
20 the single layer or two or more layers is formed between the innermost and the outermost layers so that the nickel content is continuously or intermittently increased in the direction from the innermost layer to the outermost layer. Thereby, it is possible to increase a power output.

25 The invention is achieved based on these research

results, and is characterized by:

(1) In an anode of a power generation cell for a solid oxide fuel cell, B-doped ceria particles are separately attached to a frame surface of porous nickel having a network frame structure.

(2) In an anode of a power generation cell for a solid oxide fuel cell, large diameter ceria particles are separately attached to a frame surface of porous nickel having a network frame structure, and small diameter ceria particles are separately attached between the large diameter ceria particles.

(3) In an anode of a power generation cell for a solid oxide fuel cell, the B-doped ceria particles disclosed in (1) or the B-doped ceria particles including the large diameter ceria particles and the small diameter ceria particles disclosed in (2) are expressed by a formula of $\text{Ce}_{1-m}\text{B}_m\text{O}_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$).

(4) A power generation cell for a solid oxide fuel cell includes an electrolyte which is formed of a lanthanum gallate-based oxide ion conductor, a porous cathode which is formed on a side of the electrolyte, and a porous anode which is formed on another side of the electrolyte, the anode being the anode disclosed in (1), (2), or (3).

(5) In the power generation cell for the solid oxide fuel cell disclosed in (4), the lanthanum gallate-based

oxide ion conductor is expressed by a formula of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y-z}\text{Mg}_y\text{A}_z\text{O}_3$ (A is one or more of Co, Fe, Ni, and Cu, X is 0.05 to 0.3, Y is 0 to 0.29, Z is 0.01 to 0.3, and Y+Z is 0.025 to 0.3).

5 (6) A solid oxide fuel cell includes the power generation cell for the solid oxide fuel cell disclosed in (4) or (5).

 (7) A power generation cell for a solid electrolyte fuel cell includes a solid electrolyte which is formed of a
10 lanthanum gallate-based oxide ion conductor, a porous cathode which is formed on a side of the solid electrolyte, and a porous anode which is formed on another side of the solid electrolyte. The anode includes a sintered body of B-doped ceria expressed by a formula of $\text{Ce}_{1-m}\text{B}_m\text{O}_2$ (B is one or
15 more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$) and nickel, B-doped ceria particles are separately attached to a frame surface of nickel having a porous frame structure in the sintered body, the sintered body has a nickel composition gradient so that a nickel content is increased in a thickness direction,
20 the nickel content of an innermost surface of the sintered body which is in contact with the solid electrolyte is 0.1 to 20 vol%, and the nickel content of an outermost surface of the sintered body which is farthest from the solid electrolyte is 40 to 99 vol%.

25 (8) A power generation cell for a solid electrolyte

fuel cell includes a solid electrolyte which is formed of a lanthanum gallate-based oxide ion conductor, a porous cathode which is formed on a side of the solid electrolyte, and a porous anode which is formed on another side of the solid electrolyte. The anode includes a sintered body of B-doped ceria expressed by a formula of $Ce_{1-m}B_mO_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$) and nickel, the sintered body includes a plurality of layers which has different nickel contents and in which B-doped ceria particles are separately attached to a frame surface of nickel having a porous frame structure, and the layers having the different nickel contents include an innermost layer, which is in contact with the solid electrolyte and has the nickel content of 0.1 to 20 vol%, and an outermost layer, which is separated from the solid electrolyte at least by the innermost layer and has the nickel content of 40 to 99 vol%.

(9) A power generation cell for a solid electrolyte fuel cell includes a solid electrolyte which is formed of a lanthanum gallate-based oxide ion conductor, a porous cathode which is formed on a side of the solid electrolyte, and a porous anode which is formed on another side of the solid electrolyte. The anode includes a sintered body of B-doped ceria expressed by a formula of $Ce_{1-m}B_mO_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$) and nickel, the

sintered body includes a plurality of layers which has different nickel contents and in which B-doped ceria particles are separately attached to a frame surface of nickel having a porous frame structure, the layers having
5 the different nickel contents include an innermost layer, which is in contact with the solid electrolyte and has the nickel content of 0.1 to 20 vol%, an outermost layer, which is layered so as to be farthest from the solid electrolyte and has the nickel content of 40 to 99 vol%, and an
10 intermediate layer, which is formed between the innermost and the outermost layers and has a single layer or two or more layers, and the intermediate layer including the single layer or two or more layers is layered so that the nickel content is continuously or intermittently increased in the
15 direction from the innermost layer to the outermost layer which is farthest from the solid electrolyte.

It is more preferable that the B-doped ceria particles separately attached to the surface of the porous nickel frame have two particle size distribution peaks in which
20 particle sizes are significantly different.

(f) In the power generation cell for the solid electrolyte fuel cell in which the lanthanum gallate-based oxide ion conductor is used as the solid electrolyte, the porous cathode is formed on a side of the solid electrolyte,
25 and the porous anode is formed on another side of the solid

electrolyte, the anode includes a sintered body which contains B-doped ceria expressed by the formula of $Ce_{1-m}B_mO_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$) and nickel. In the sintered body, as shown in Fig. 1, B-doped ceria particles, which are expressed by the formula of $Ce_{1-m}B_mO_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$) and have an average particle size of 0.2 to 0.6 μm (hereinafter, the B-doped ceria particle having the average particle size of 0.2 to 0.6 μm will be referred to as "large diameter ceria particle"), are separately attached to the surface of nickel of the porous frame structure, and B-doped ceria particles, which are expressed by the formula of $Ce_{1-m}B_mO_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$) and have an average particle size of 0.01 to 0.09 μm (hereinafter, the B-doped ceria particle having the average particle size of 0.01 to 0.09 μm will be referred to as "small diameter ceria particle"), are separately attached between the large diameter ceria particles. Furthermore, the sintered body has the nickel composition gradient, thus the nickel content is increased in a thickness direction. The nickel content of the innermost surface of the anode which is in contact with the solid electrolyte is 0.1 to 20 vol%, and the nickel content of the outermost surface of the anode is 40 to 99 vol%. Thereby, it is possible to increase a power output.

(g) In the power generation cell for the solid electrolyte fuel cell in which the lanthanum gallate-based oxide ion conductor is used as the solid electrolyte, the porous cathode is formed on a side of the solid electrolyte, and the porous anode is formed on another side of the solid electrolyte, the anode includes the sintered body which contains B-doped ceria expressed by the formula of $Ce_{1-m}B_mO_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$) and nickel. As shown in Fig. 1, the sintered body includes a plurality of layers having different nickel contents, in which the large diameter ceria particles are separately attached to the surface of nickel of the porous frame structure and the small diameter ceria particles are separately attached between the large diameter ceria particles. A plurality of layers includes at least the innermost layer, which has the nickel content of 0.1 to 20 vol% and is in contact with the solid electrolyte, and the outermost layer, which has the nickel content of 40 to 99 vol% and is separated from the solid electrolyte at least by the innermost layer. Thereby, it is possible to increase a power output.

(h) The intermediate layer including a single layer or two or more layers is formed between the innermost and the outermost layers having the different nickel contents disclosed in (e). The nickel content of the innermost layer

is 0.1 to 20 vol%, and the nickel content of the outermost layer is 40 to 99 vol%. The intermediate layer including the single layer or two or more layers is formed between the innermost and the outermost layers so that the nickel
5 content is continuously or intermittently increased in the direction from the innermost layer to the outermost layer. Thereby, it is possible to increase a power output.

Therefore, the invention is characterized by:

(10) A power generation cell for a solid electrolyte
10 fuel cell includes a solid electrolyte which is formed of a lanthanum gallate-based oxide ion conductor, a porous cathode which is formed on a side of the solid electrolyte, and a porous anode which is formed on another side of the solid electrolyte. The anode includes a sintered body of B-
15 doped ceria expressed by a formula of $Ce_{1-m}B_mO_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$) and nickel, the sintered body includes B-doped ceria particles, which have an average particle size of 0.2 to 0.6 μm (large diameter ceria particle) and which are separately attached to a frame
20 surface of nickel having a porous frame structure, and B-doped ceria particles, which have an average particle size of 0.01 to 0.09 μm (small diameter ceria particle) and which are separately attached between the large diameter ceria particles, the sintered body also has a nickel composition
25 gradient so that the nickel content is increased in a

thickness direction, the nickel content of an innermost surface of the sintered body which is in contact with the solid electrolyte is 0.1 to 20 vol%, and the nickel content of an outermost surface of the sintered body which is
5 farthest from the solid electrolyte is 40 to 99 vol%.

(11) A power generation cell for a solid electrolyte fuel cell includes a solid electrolyte which is formed of a lanthanum gallate-based oxide ion conductor, a porous cathode which is formed on a side of the solid electrolyte,
10 and a porous anode which is formed on another side of the solid electrolyte. The anode includes a sintered body of B-doped ceria expressed by a formula of $Ce_{1-m}B_mO_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$) and nickel, the sintered body includes a plurality of layers which has
15 different nickel contents and in which large diameter ceria particles are separately attached to a frame surface of nickel having a porous frame structure and small diameter ceria particles are separately attached between the large diameter ceria particles, and the layers having the
20 different nickel contents include an innermost layer, which is in contact with the solid electrolyte and has the nickel content of 0.1 to 20 vol%, and an outermost layer, which is separated from the solid electrolyte at least by the innermost layer and has the nickel content of 40 to 99 vol%.

25 (12) A power generation cell for a solid electrolyte

fuel cell includes a solid electrolyte which is formed of a lanthanum gallate-based oxide ion conductor, a porous cathode which is formed on a side of the solid electrolyte, and a porous anode which is formed on another side of the solid electrolyte. The anode includes a sintered body of B-doped ceria expressed by a formula of $Ce_{1-m}B_mO_2$ (B is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$) and nickel, the sintered body includes a plurality of layers which has different nickel contents and in which large diameter ceria particles are separately attached to a frame surface of nickel having a porous frame structure and small diameter ceria particles are separately attached between the large diameter ceria particles, the layers having the different nickel contents include an innermost layer, which is in contact with the solid electrolyte and has the nickel content of 0.1 to 20 vol%, an outermost layer, which is layered so as to be farthest from the solid electrolyte and has the nickel content of 40 to 99 vol%, and an intermediate layer, which is formed between the innermost and the outermost layers and has a single layer or two or more layers, and the intermediate layer including the single layer or two or more layers is layered so that the nickel content is continuously or intermittently increased in the direction from the innermost layer to the outermost layer which is farthest from the solid electrolyte.

It is preferable that the innermost layer be as slim as possible, the thickness of the innermost layer is 0.5 to 5 μm , and it is preferable that the thickness of the outermost layer be 10 to 50 μm . Furthermore, it is preferable that
5 the lanthanum gallate-based oxide ion conductor be expressed by the formula of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y-z}\text{Mg}_y\text{A}_z\text{O}_3$ (A is one or more of Co, Fe, Ni, and Cu, X is 0.05 to 0.3, Y is 0 to 0.29, Z is 0.01 to 0.3, and Y+Z is 0.025 to 0.3). Accordingly, the invention is characterized by:

10 (13) In the power generation cell for the solid electrolyte fuel cell disclosed in (8), (9), (11), or (12), a thickness of the innermost layer is 0.5 to 5 μm , and a thickness of the outermost layer is 10 to 50 μm .

(14) In the power generation cell for the solid
15 electrolyte fuel cell disclosed in (7), (8), (9), (10), (11), (12), or (13), the lanthanum gallate-based oxide ion conductor is expressed by the formula of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y-z}\text{Mg}_y\text{A}_z\text{O}_3$ (A is one or more of Co, Fe, Ni, and Cu, X is 0.05 to 0.3, Y is 0 to 0.29, Z is 0.01 to 0.3, and Y+Z is 0.025 to 0.3).

20 In an anode of a power generation cell for a solid electrolyte fuel cell according to an aspect of the invention, B-doped ceria particles are separately attached to a surface of nickel of a porous frame structure. It is possible to improve characteristics of the solid electrolyte
25 fuel cell using the anode. The reason for this is as

follows. That is to say, if the anode, in which the B-doped ceria particles are separately attached to the surface of nickel of the porous frame structure, is used, when the solid electrolyte fuel cell is operated, nickel is locally
5 thermally expanded due to a high heating value, and the volume of ceria is reduced because the valence of ceria is changed from +3 to +4. However, since the B-doped ceria particles are separated from each other, there is little influence resulting from a difference in expansion, and B-
10 doped ceria is not separated from nickel.

Furthermore, if the B-doped ceria particles are separately attached to the surface of nickel, growth of the nickel particles is suppressed, thus ~~an increase~~ decrease of an exposure area of nickel metal resulting from the
15 growth of the nickel particles is obstructed. Accordingly, reduction of the distribution density of the B-doped ceria particles, which are attached to the surface of nickel of the porous frame structure, is suppressed, thereby it is possible to prevent characteristics of the solid electrolyte
20 fuel cell from deteriorating, caused by the reduction of reaction area of hydrogen used as fuel.

In this connection, in an anode of a conventional solid electrolyte fuel cell shown in Fig. 3, since ceria particles forms a network to be connected to each other, a surface of
25 nickel of a porous frame structure is coated with ceria, and

an exposure area of the surface of nickel is reduced to decrease conductivity. Additionally, the anode is vulnerable to the influence by a difference in expansion and has an internal strain caused by tensile stress of ceria forming the network. Further, ceria is separated from nickel, thus it is impossible to obtain desirable characteristics of the solid electrolyte fuel cell.

Fig. 1 illustrates a more preferable structure of an anode of a power generation cell for a solid electrolyte fuel cell according to an aspect of the invention, which is disclosed in (2), and (4) to (6). As shown in Fig. 1, in the anode of the power generation cell for the solid electrolyte fuel cell according to the aspect of the invention, large diameter ceria particles including B-doped ceria are separately attached to the surface of nickel of the porous frame structure, and B-doped small diameter ceria particles are separately attached between the large diameter ceria particles which are separately attached. When the power generation cell including the anode having the above-mentioned structure is used, it is possible to improve characteristics of the solid electrolyte fuel cell.

The reason for this is as follows. That is to say, if the B-doped large diameter ceria particles shown in Fig. 1 are separately attached to the surface of nickel of the porous frame structure, and if the B-doped small diameter

ceria particles are separately attached between the B-doped large diameter ceria particles, B-doped ceria particles are ~~densely attached to~~ dense on the surface of nickel of the porous frame structure, thus the reaction area to hydrogen
5 used as fuel is increased. Additionally, when the solid electrolyte fuel cell is operated, nickel of the anode is locally thermally expanded due to a high heating value, and the volume of ceria is reduced because the valence of ceria is changed from +3 to +4. However, since the B-doped ceria
10 particles do not form a network in the microstructure shown in Fig. 1, there is little influence caused by a difference in expansion, thus B-doped ceria is not separated from nickel.

Furthermore, in the microstructure shown in Fig. 1,
15 since the B-doped small diameter ceria particles are separately attached to the surface of nickel between the large diameter ceria particles, exposure of the surface of nickel of the porous frame structure is assured, thus conductivity is not reduced. Accordingly, characteristics
20 of the power generation cell are improved.

Additionally, the reason why the nickel content of the innermost surface or the innermost layer is 0.1 to 20 vol% in the anode formed in the power generation cell for the solid electrolyte fuel cell according to the aspect of the
25 invention is as follows. If the nickel content of the

innermost surface or the innermost layer is less than 0.1 vol%, it is impossible to obtain desirable strength because the amount of nickel constituting the frame is very small. Additionally, in case the nickel content of the innermost surface or the innermost layer is more than 20 vol%, nickel is present in the very large amount, thus this case is undesirable because characteristics of the anode are significantly reduced. Furthermore, the reason why the nickel content of the outermost surface or the outermost layer farthest from the solid electrolyte is 40 to 99 vol% is as follows. In case the nickel content is less than 40 vol%, it is impossible to obtain desirable strength required in the anode. In case the nickel content is more than 99 vol%, desirable strength is obtained, but this case is undesirable because characteristics of the anode are significantly reduced.

Furthermore, in the anode formed in the power generation cell for the solid electrolyte fuel cell according to the aspect of the invention, which is disclosed in (8), (9), (11), and (12), the thickness of the innermost layer is limited to 0.5 to 5 μm . The reason for this is as follows. The slimmer the innermost layer is, the more desirable the anode is. However, in order to form the innermost layer at low cost, the thickness must be 0.5 μm or more. If the thickness is required to be smaller, cost

becomes very high. In the case of the innermost layer having the thickness larger than 5 μm , since the layer is very thick, characteristics of the anode are reduced, thus this case is undesirable.

5 Additionally, the reason why the thickness of the outermost layer, which is farthest from the solid electrolyte, is limited to 10 to 50 μm is as follows. In case the thickness is less than 10 μm , a surface area of Ni is small and it is impossible to obtain a sufficient
10 effective electrode reaction area, thus this case is undesirable. Additionally, in case the thickness of the outermost layer is more than 50 μm , stress occurs in the cell due to expansion of Ni, and diffusion resistance of fuel gas is increased in the electrode, thus this case is
15 undesirable.

The invention has the following characters.

The power generation cell for the solid electrolyte fuel cell according to the aspect of the invention includes the lanthanum gallate-based oxide ion conductor used as the
20 solid electrolyte. The lanthanum gallate-based oxide ion conductor is expressed by the formula of $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y-z}\text{Mg}_y\text{A}_z\text{O}_3$ (A is one or more of Co, Fe, Ni, and Cu, X is 0.05 to 0.3, Y is 0 to 0.29, Z is 0.01 to 0.3, and Y+Z is 0.025 to 0.3). Furthermore, the power generation cell includes the anode
25 having B-doped ceria expressed by the formula of $\text{Ce}_{1-m}\text{B}_m\text{O}_2$ (B

is one or more of Sm, Gd, Y, and Ca, and $0 < m \leq 0.4$), and nickel. The B-doped ceria particles are separately attached to the surface of nickel of the porous frame structure forming the network. B-doped ceria is compatible with the
5 lanthanum gallate-based solid electrolyte. If B-doped ceria scorches and sticks to the lanthanum gallate-based solid electrolyte at 1350°C or less, the resulting structure desirably acts as the anode, thus it is possible to produce the power generation cell for the solid electrolyte fuel
10 cell having high characteristics.

In the power generation cell for the solid electrolyte fuel cell according to the aspect of the invention, the anode is characterized in that the B-doped ceria particles are separately attached to the surface of nickel of the
15 porous frame structure as described above. It is more preferable that the B-doped ceria particles, which are separately attached to the surface of nickel of the porous frame structure, include the large and the small diameter ceria particles, and that the fine small diameter ceria
20 particles are attached to the surface of nickel between the large diameter ceria particles. The average particle size of the large diameter ceria particles is preferably set to 0.2 to 0.6 μm , and may be within a range (0.1 to 2 μm) of the average particle size of the known B-doped ceria. It is
25 more preferable that the average particle size of the small

diameter ceria particles be significantly fine 0.01 to 0.09 μm .

The reason why the average particle size of the small diameter ceria particles is set to 0.01 to 0.09 μm is as follows. It is difficult to form small diameter ceria particles which has the average particle size of less than 0.01 μm and are separated from each other. Additionally, if the average particle size is more than 0.09 μm , it is difficult to separately attach the small diameter ceria particles between the large diameter ceria particles. Meanwhile, the average particle sizes of the large diameter ceria particles and the small diameter ceria particles may be obtained by the image analysis.

A solid oxide fuel cell having a power generation cell, in which an anode of the aspect of the invention is provided, is capable of being operated at low temperatures, and it is possible to realize compactness and high efficiency of a generating module of the fuel cell.

Brief Description of the Drawings

Fig. 1 illustrates a structure of an anode ~~of an aspect of~~ in accordance with the invention.

Fig. 2 is a scanning electron microscope picture of the structure of the anode ~~of the aspect of the invention;~~

Fig. 3 illustrates a structure of a conventional anode;

Fig. 4 illustrates a solid electrolyte fuel cell;

Fig. 5 illustrates a power generation cell of a solid electrolyte fuel cell according to another aspect of the invention; and

5 Fig. 6 illustrates a power generation cell of a solid electrolyte fuel cell according to still another aspect of the invention.

~~Best Mode for Carrying Out the Invention~~ Detailed description

10 of the preferred embodiments

[Example 1]

First, a method of preparing a crude material used to produce a power generation cell will be described.

(a) Production of lanthanum gallate-based electrolyte
15 crude powder:

Reagent-level pulverulent bodies of lanthanum oxide, strontium carbonate, gallium oxide, magnesium oxide, and cobalt oxide were prepared, weighed so as to form a composition expressed by $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05})\text{O}_3$, mixed
20 using a ball mill, and heated at 1350°C for 3 hours in the air to form lumps of sintered bodies. The sintered body was coarsely pulverized using a hammer mill, and finely pulverized using the ball mill to produce lanthanum gallate-based electrolyte crude powder having the average particle
25 size of 1.3 μm .

(b) Production of an ethanol solution containing ultrafine samarium-doped ceria (hereinafter, referred to as SDC) powder:

1 mol/L sodium hydroxide aqueous solution was dropped
5 on a mixed aqueous solution of 8 parts of 0.5 mol/L cerium nitrate aqueous solution and 2 parts of 0.5 mol/L samarium nitrate aqueous solution while the mixed aqueous solution was agitated to coprecipitate cerium oxide and samarium oxide. Next, the produced powder was precipitated using a
10 centrifugal separator, a supernatant liquid was discarded, distilled water was added, agitation and rinsing were conducted, re-precipitation was conducted using the centrifugal separator, and this procedure was repeated six times to carry out rinsing. Next, precipitation was
15 conducted using the centrifugal separator, ethanol was added, agitation was conducted, re-precipitation was conducted using the centrifugal separator, and this procedure was repeated three times to substitute water of the solution by ethanol and thus produce an ethanol solution containing
20 ultrafine SDC powder. A portion of the resulting ethanol solution containing the ultrafine SDC powder was drawn, and the average particle size of the ultrafine powder of ceria was 0.04 μm , as a result of measurement using a laser diffraction method.

25 (b-1) Production of doped large diameter ceria powder:

1 mol/L sodium hydroxide aqueous solution was dropped on a mixed aqueous solution of 8 parts of 0.5 mol/L cerium nitrate aqueous solution and 2 parts of 0.5 mol/L samarium nitrate aqueous solution while the mixed aqueous solution was agitated to coprecipitate cerium oxide and samarium oxide. After filtration, agitation, rinsing, and filtration were repeatedly carried out six times using pure water to achieve washing so as to produce coprecipitate powder of cerium oxide and samarium oxide. The coprecipitate powder was heated at 1000°C for 3 hours in the air to produce doped ceria powder 1 having a composition of $(\text{Ce}_{0.8}\text{Sm}_{0.2})\text{O}_2$ and the average particle size of about 0.8 μm .

(c) Production of nickel oxide powder:

1 mol/L sodium hydroxide aqueous solution was dropped on 1 mol/L nickel nitrate aqueous solution while the solution was agitated to precipitate nickel hydroxide. After nickel hydroxide was filtered, agitation, rinsing, and filtration were repeatedly carried out six times using pure water to achieve washing, and the resulting substance was heated at 900°C for 3 hours in the air to produce nickel oxide powder having the average particle size of 1.1 μm .

(d) Production of samarium strontium cobaltite-based cathode crude powder:

Reagent-level pulverulent bodies of samarium oxide, strontium carbonate, and cobalt oxide were prepared, weighed

so as to form a composition expressed by $(\text{Sm}_{0.5}\text{Sr}_{0.5})\text{CoO}_3$, mixed using a ball mill, and heated at 1000°C for 3 hours in the air. The resulting pulverulent bodies were finely pulverized using the ball mill to produce samarium strontium
5 cobaltite-based cathode crude powder having the average particle size of $1.1\ \mu\text{m}$.

Next, the power generation cell was produced through the following procedure using the produced crude substance. First, the lanthanum gallate-based electrolyte crude powder
10 produced in (a) was mixed with the organic binder solution, in which polyvinyl butyral and N-dioctyl phthalate were dissolved in the toluene-ethanol solvent, to form slurry. The slurry was shaped into a thin plate using a doctor blade method, cut in a circular form, and heated at 1450°C for 4
15 hours in the air to conduct sintering, thereby producing a disk-shaped lanthanum gallate-based electrolyte having ~~the~~a thickness of $200\ \mu\text{m}$ and ~~the~~a diameter of 120 mm. The nickel oxide powder produced in (c) was mixed with the ethanol solution containing the ultrafine SDC powder
20 produced in (b) so that the volume ratio of nickel oxide to SDC was 60:40, and the resulting mixture was mixed with the organic binder solution, in which polyvinyl butyral and N-dioctyl phthalate were dissolved in the toluene-ethanol solvent, to form slurry. A slurry film was formed on the
25 disk-shaped lanthanum gallate-based electrolyte through a

screen printing method using the slurry so that the thickness was 30 μm , dried, and heated at 1250°C for 3 hours in the air. Thereby, the anode was shaped, scorched and stuck to the disk-shaped lanthanum gallate-based electrolyte.

5 Meanwhile, the powder produced using the wet (coprecipitation) process was the dispersed ultrafine powder (nanoparticles). However, when the powder was dried, the particles were rapidly agglomerated. Accordingly, in order to mix the fine powder with nickel oxide to form the slurry
10 without the agglomeration, the ethanol solution containing the ultrafine SDC powder was used. After the shaping, SDC was agglomerated on the surface of the nickel oxide powder during the drying to realize a separated ceria state. The resulting ceria was sintered to obtain the anode ~~of an~~
15 ~~aspect of the invention~~. A portion of the microstructure of the above-mentioned anode ~~according to the aspect of the in~~
accordance with the invention was observed using a scanning electron microscope, and the picture of the structure taken using the scanning electron microscope ~~was~~ is shown in Fig.
20 2. The particle sizes of the large diameter ceria particles and the small diameter ceria particles, which ~~were~~ are separately attached to the surface of nickel of the porous frame structure shown in the picture, were measured using the image analysis method. In result, it was confirmed that
25 the samarium-doped small diameter ceria particles having ~~the~~

an average particle size of 0.05 μm were separately attached between the samarium-doped large diameter ceria particles having the average particle size of 0.4 μm .

Furthermore, the samarium strontium cobaltite-based
5 cathode crude powder produced in (d) was mixed with the organic binder solution, in which polyvinyl butyral and N-diethyl phthalate were dissolved in the toluene-ethanol solvent, to form slurry. The slurry was shaped on a side of the lanthanum gallate-based electrolyte having another side,
10 to which the anode scorched and stuck, using ~~the~~ a screen printing method so that the thickness was 30 μm , dried, and heated at 1100°C for 5 hours in the air, thus the cathode was formed, scorched and stuck to the electrolyte.

Thereby, the power generation cell for ~~the~~ a solid
15 electrolyte fuel cell ~~according to the aspect of the invention~~ (hereinafter, referred to as "the power generation cell of the aspect of the invention"), which included ~~as~~ s the solid electrolyte, the anode, and the cathode, was produced. An anode collector, which had the thickness of 1 mm and
20 included porous Ni, was layered on the anode of the power generation cell of the aspect of the invention. Furthermore, a cathode collector, which had the thickness of 1.2 mm and included porous Ag, was layered on the cathode of the power generation cell of the aspect of the invention. Separators
25 were layered on the anode collector and the cathode

collector to produce the solid electrolyte fuel cell of the aspect of the invention shown in Fig. 4.

[Conventional example]

For comparison, the conventional solid electrolyte fuel
5 cell was produced through the following procedure. First,
1N-nickel nitrate aqueous solution, 1N-cerium nitrate
aqueous solution, and 1N-samarium nitrate aqueous solution
were prepared, weighed so that the volume ratio of NiO to
(Ce_{0.8}Sm_{0.2})O₂ was 60:40, and mixed with each other. The
10 resulting solution was converted into a vapor using a
vaporizer, and air was fed into a tube-type furnace as a
carrier gas. Heating was conducted at 1000°C to produce
composite oxide powder in which the volume ratio of NiO to
(Ce_{0.8}Sm_{0.2})O₂ was 60:40. The composite oxide powder was used
15 to produce slurry, and the slurry was applied on a side of
the lanthanum gallate-based solid electrolyte produced in
example 1 and sintered to form the anode. Furthermore, the
cathode was formed using the same procedure as in example 1
to produce the power generation cell. As shown in Fig. 3,
20 the anode formed in the power generation cell had a network
structure in which samarium-doped ceria (SDC) surrounded the
surface of nickel of the porous frame structure. The anode
collector was layered on a side of the power generation cell,
and the separator was layered on the anode collector.
25 Additionally, the cathode collector was layered on another

side of the conventional power generation cell, and the separator was layered on the cathode collector to produce the conventional solid electrolyte fuel cell shown in Fig. 4.

The A power generation test was conducted using the solid electrolyte fuel cell of the aspect of the invention and the conventional solid electrolyte fuel cell under the following conditions, and the results are described in Table 1.

<Power generation test>

Temperature: 750°C

Fuel gas: hydrogen

Flow rate of fuel gas: 1.02 L/min (=9 cc/min/cm²)

Oxidant gas: air

Flow rate of oxidant gas: 5.1 L/min (=45 cc/min/cm²)

Electric power was generated under the above-mentioned power generation conditions, and load current density, open circuit voltage, fuel utilization, cell voltage, output, output density, and generating efficiency were measured. The results are described in Table 1.

[Table 1]

Type	load current density <u>Open circuit voltage</u> (A/cm ²)	Fuel utilization (%)	Cell voltage (V)	Output (W)	Output density (W/cm ²)	Generating efficiency LHV (%)
Solid electrolyte fuel cell	1.015	80	0.695	68.3	0.604	37.9

of the aspect of the invention						
Conventional solid electrolyte fuel cell	0.90	70	0.533	54.2	0.480	30.1

From the results of Table 1, it is confirmed that, even though the solid electrolyte fuel cell of the aspect of the invention and the conventional solid electrolyte fuel cell have the same structure with the exception of the anode, the solid electrolyte fuel cell of ~~the aspect of the invention~~ have the has excellent load current density open circuit voltage, fuel utilization, cell voltage, output, output density, and generating efficiency in comparison with the conventional solid electrolyte fuel cell.

[Example 2]

<Production of the power generation cell>

Production of lanthanum gallate-based solid electrolyte crude powder:

Reagent-level pulverulent bodies of lanthanum oxide, strontium carbonate, gallium oxide, magnesium oxide, and cobalt oxide were prepared, weighed so as to form a composition expressed by $(\text{La}_{0.8}\text{Sr}_{0.2})(\text{Ga}_{0.8}\text{Mg}_{0.15}\text{Co}_{0.05})\text{O}_3$, mixed using a ball mill, and heated at 1350°C for 3 hours in the air to form lumps of sintered bodies. The sintered body was

coarsely pulverized using a hammer mill, and finely pulverized using ~~the~~a ball mill to produce lanthanum gallate-based solid electrolyte crude powder having ~~the~~an average particle size of 1.3 μm .

5 Production of an ethanol solution containing ultrafine samarium-doped ceria powder:

 Next, 1 mol/L sodium hydroxide aqueous solution was dropped on a mixed aqueous solution of 8 parts of 0.5 mol/L cerium nitrate aqueous solution and 2 parts of 0.5 mol/L
10 samarium nitrate aqueous solution while the mixed aqueous solution was agitated to coprecipitate cerium oxide and samarium oxide. Next, the produced powder was precipitated using a centrifugal separator, a supernatant liquid was discarded, distilled water was added, agitation and rinsing
15 were conducted, re-precipitation was conducted using the centrifugal separator, and this procedure was repeated six times to carry out rinsing. Next, precipitation was conducted using the centrifugal separator, ethanol was added, agitation was conducted, re-precipitation was conducted
20 using the centrifugal separator, and this procedure was repeated three times to substitute water of the solution by ethanol and thus produce an ethanol solution containing ultrafine samarium-doped ceria (hereinafter, referred to as "SDC") powder. A portion of the resulting ethanol solution
25 containing the ultrafine SDC powder was drawn, and the

average particle size of the ultrafine powder of ceria was 0.04 μm , as a result of measurement using a laser diffraction method.

Production of samarium-doped ceria powder:

5 1 mol/L sodium hydroxide aqueous solution was dropped on a mixed aqueous solution of 8 parts of 0.5 mol/L cerium nitrate aqueous solution and 2 parts of 0.5 mol/L samarium nitrate aqueous solution while the mixed aqueous solution was agitated to coprecipitate cerium oxide and samarium
10 oxide. After filtration, agitation, rinsing, and filtration were repeatedly carried out six times using pure water to achieve washing so as to produce coprecipitate powder of cerium oxide and samarium oxide. The coprecipitate powder was heated at 1000°C for 3 hours in the air to produce SDC
15 powder having a composition of $(\text{Ce}_{0.8}\text{Sm}_{0.2})\text{O}_2$ and the average particle size of about 0.8 μm .

Production of nickel oxide powder:

1 mol/L sodium hydroxide aqueous solution was dropped on 1 mol/L nickel nitrate aqueous solution while the
20 solution was agitated to precipitate nickel hydroxide. After nickel hydroxide was filtered, agitation, rinsing, and filtration were repeatedly carried out six times using pure water to achieve washing, and the resulting substance was heated at 900°C for 3 hours in the air to produce nickel
25 oxide powder having the average particle size of 1.1 μm .

Production of samarium strontium cobaltite-based
cathode crude powder:

Reagent-level pulverulent bodies of samarium oxide,
strontium carbonate, and cobalt oxide were prepared, weighed
5 so as to form a composition expressed by $(\text{Sm}_{0.5}\text{Sr}_{0.5})\text{CoO}_3$,
mixed using a ball mill, and heated at 1000°C for 3 hours in
the air. The resulting pulverulent bodies were finely
pulverized using the ball mill to produce samarium strontium
cobaltite-based cathode crude powder having the average
10 particle size of 1.1 μm .

Production of lanthanum gallate-based solid
electrolyte:

The lanthanum gallate-based solid electrolyte crude
powder was mixed with the organic binder solution, in which
15 polyvinyl butyral and N-diethyl phthalate were dissolved in
the toluene-ethanol solvent, to form slurry. The slurry was
shaped into a thin plate using a doctor blade method, cut in
a circular form, and heated at 1450°C for 4 hours in the air
to conduct sintering, thereby producing a disk-shaped
20 lanthanum gallate-based solid electrolyte having the
thickness of 200 μm and the diameter of 120 mm.

Shaping, scorching and sticking of the anode:

The nickel oxide powder was mixed with the SDC powder in ~~the~~
a volume ratio of 10:90, and the resulting mixture was mixed
25 with the organic binder solution, in which polyvinyl butyral

and N-dioctyl phthalate were dissolved in the toluene-ethanol solvent, to form slurry. The slurry was applied on a side of the lanthanum gallate-based solid electrolyte using the screen printing method so that the average
5 thickness was 1 μm , and dried to form a first green layer.

Furthermore, the nickel oxide powder was mixed with the ethanol solution containing the ultrafine SDC powder so that the volume ratio of nickel oxide to SDC was 60:40, and the resulting mixture was mixed with the organic binder solution,
10 in which polyvinyl butyral and N-dioctyl phthalate were dissolved in the toluene-ethanol solvent, to form slurry. A slurry layer was formed on the dried first green layer through the screen printing method using the slurry so that the thickness was 30 μm , and dried to form a second green
15 layer.

Next, the lanthanum gallate-based solid electrolyte, which includes a plurality of green layers having the first and the second green layers on a side thereof, was heated at 1250°C for 3 hours in the air so as to cause the anode
20 including the anode innermost layer and the anode outermost layer shown in Fig. 5 to scorch and stick to the side of the lanthanum gallate-based solid electrolyte.

Meanwhile, the powder produced using the coprecipitation process was the dispersed ultrafine powder
25 (nanoparticles). However, when the powder was dried, the

particles were rapidly agglomerated. Accordingly, in order to mix the fine powder with nickel oxide to form the slurry without the agglomeration, the ethanol solution containing the ultrafine SDC powder was used. After the shaping, SDC
5 was agglomerated on the surface of the nickel oxide powder during ~~the~~ drying to realize a separated ceria state. The resulting ceria was sintered to obtain the anode of another aspect of the invention. A portion of the microstructure of the above-mentioned anode according to the aspect of the
10 invention was observed using a scanning electron microscope, and the picture of the structure taken using the scanning electron microscope ~~was~~ is shown in Fig. 2. The particle sizes of the large diameter ceria particles and the small diameter ceria particles, which ~~were~~ are separately attached
15 to the surface of nickel of the porous frame structure shown in the picture, were measured using the image analysis method. In result, it was confirmed that the samarium-doped small diameter ceria particles having the average particle size of 0.05 μ m were separately attached between the
20 samarium-doped large diameter ceria particles having the average particle size of 0.4 μ m.

Shaping, scorching and sticking of the cathode:

The samarium strontium cobaltite-based cathode crude powder was mixed with the organic binder solution, in which
25 polyvinyl butyral and N-dioctyl phthalate were dissolved in

the toluene-ethanol solvent, to form slurry. The slurry was shaped on a side of the lanthanum gallate-based solid electrolyte using ~~the~~ a screen printing method so that the thickness was 30 μm , dried, and heated at 1100°C for 5 hours in the air, thus the cathode shown in Fig. 5 was shaped, scorched and stuck to the electrolyte.

Thereby, the power generation cell 1 for ~~the~~ a solid electrolyte fuel cell ~~according to the aspect of the invention (hereinafter, referred to as "the power generation cell of the aspect of the invention")~~, which included the solid electrolyte, the anode, and the cathode, was produced as shown in Fig. 5. An anode collector, which had the thickness of 1 mm and included porous Ni, was layered on the anode of the power generation cell 1 ~~of the aspect of the invention~~. Furthermore, a cathode collector, which had the thickness of 1.2 mm and included porous Ag, was layered on the cathode of the power generation cell ~~of the aspect of the invention~~. Separators were layered on the anode collector and the cathode collector to produce the solid electrolyte fuel cell 1 ~~of the aspect of the invention shown as in Fig. 4~~.

For comparison, the conventional solid electrolyte fuel cell was produced through the following procedure. First, 1N-nickel nitrate aqueous solution, 1N-cerium nitrate aqueous solution, and 1N-samarium nitrate aqueous solution

were prepared, weighed so that the volume ratio of NiO to
(Ce_{0.8}Sm_{0.2})O₂ was 60:40, and mixed with each other. The
resulting solution was converted into a vapor using a
vaporizer, and air was fed into a tube-type furnace as a
5 carrier gas. Heating was conducted at 1000°C to produce
composite oxide powder in which the volume ratio of NiO to
(Ce_{0.8}Sm_{0.2})O₂ was 60:40. The composite oxide powder was used
to produce slurry, and the slurry was applied on a side of
the lanthanum gallate-based solid electrolyte produced in
10 the example and sintered to form the anode. Furthermore,
the cathode was formed to produce the power generation cell.
As shown in Fig. 3, the anode formed in the power generation
cell had a network structure in which SDC surrounded the
surface of nickel of the porous frame structure. The anode
15 collector was layered on a side of the power generation cell,
and the separator was layered on the anode collector.
Additionally, the cathode collector was layered on another
side of the conventional power generation cell, and the
separator was layered on the cathode collector to produce
20 the conventional solid electrolyte fuel cell shown in Fig. 4.

The power generation test was conducted using the solid
electrolyte fuel cell 1 of the aspect of the invention and
the conventional solid electrolyte fuel cell under the
following conditions.

25 <Power generation test>

Temperature: 750°C

Fuel gas: hydrogen

Flow rate of fuel gas: 1.02 L/min (=9 cc/min/cm²)

Oxidant gas: air

5 Flow rate of oxidant gas: 5.1 L/min (=45 cc/min/cm²)

Electric power was generated under the above-mentioned power generation conditions, and ~~load-current-density~~open circuit voltage, fuel utilization, cell voltage, output, output density, and generating efficiency were measured.

10 The results are described in Table 12.

[Table 2]

Type	Open circuit voltage (V)	Fuel utilization (%)	Cell voltage (V)	Output (W)	Output density (W/cm ²)	Generating efficiency LHV (%)
Solid electrolyte fuel cell 1 of the aspect of the invention	1.015	80	0.624	73.1	0.646	40.0
Conventional solid electrolyte fuel cell	0.90	70	0.472	54.3	0.480	30.2

From the results of Table 2, it is confirmed that, even though the solid electrolyte fuel cell 1 of the aspect of the invention and the conventional solid electrolyte fuel cell have the same structure with the exception of the anode, the solid electrolyte fuel cell 1 of the aspect of the invention have the excellent ~~load current density~~open circuit voltage, fuel utilization, cell voltage, output, output density, and generating efficiency in comparison with the conventional solid electrolyte fuel cell.

[Example 3]

The nickel oxide powder prepared in example 2 was mixed with the SDC powder in the volume ratio of 10:90, and the resulting mixture was mixed with the organic binder solution, in which polyvinyl butyral and N-dioctyl phthalate were dissolved in the toluene-ethanol solvent, to form slurry.

The slurry was applied on a side of the lanthanum gallate-based solid electrolyte using the screen printing method so that the average thickness was 1 μm , and dried to form a first green layer.

5 Furthermore, the nickel oxide powder was mixed with the ethanol solution containing the ultrafine SDC powder so that the volume ratio of nickel oxide to SDC was 35:65, and the resulting mixture was mixed with the organic binder solution, in which polyvinyl butyral and N-dioctyl phthalate were
10 dissolved in the toluene-ethanol solvent, to form slurry. A slurry layer was formed on the dried first green layer through the screen printing method using the slurry so that the thickness was 1 μm , and dried to form an intermediate green layer.

15 Furthermore, the nickel oxide powder was mixed with the ethanol solution containing the ultrafine SDC powder so that the volume ratio of nickel oxide to SDC was 60:40, and the resulting mixture was mixed with the organic binder solution, in which polyvinyl butyral and N-dioctyl phthalate were
20 dissolved in the toluene-ethanol solvent, to form slurry. A slurry layer was formed on the dried intermediate green layer through the screen printing method using the slurry so that the thickness was 20 μm , and dried to form a second green layer.

25 Next, the lanthanum gallate-based solid electrolyte,

which includes a plurality of green layers having the first green layer, the intermediate green layer, and the second green layers on a side thereof, was heated at 1250°C for 3 hours in the air so as to cause the anode including the
5 anode innermost layer, the anode intermediate layer, and the anode outermost layer shown in Fig. 6 to scorch and stick to the side of the lanthanum gallate-based solid electrolyte.

It was confirmed that the anode, which was formed through the scorching and the sticking, had a structure
10 where the samarium-doped small diameter ceria particles having the average particle size of 0.05 μm were separately attached between the samarium-doped large diameter ceria particles having the average particle size of 0.4 μm .

The procedure of example 2 was repeated to cause the
15 solid electrolyte and the cathode to scorch and stick, except that the anode scorched and stuck as described above, thereby producing a power generation cell 2 including the solid electrolyte, the anode, and the cathode according to still another aspect of the invention. An anode collector,
20 which had the thickness of 1 mm and included porous Ni, was layered on the anode of the power generation cell 2 of the aspect of the invention. Furthermore, a cathode collector, which had the thickness of 1.2 mm and included porous Ag, was layered on the cathode of the power generation cell 2 of
25 the aspect of the invention. Separators were layered on the

anode collector and the cathode collector to produce a solid electrolyte fuel cell 2 of the aspect of the invention.

The power generation test was conducted using the solid electrolyte fuel cell 2 of the aspect of the invention under
5 the following conditions.

<Power generation test>

Temperature: 750°C

Fuel gas: hydrogen

Flow rate of fuel gas: 1.02 L/min (=9 cc/min/cm²)

10 Oxidant gas: air

Flow rate of oxidant gas: 5.1 L/min (=45 cc/min/cm²)

Electric power was generated under the above-mentioned power generation conditions, and ~~load current density~~open circuit voltage, fuel utilization, cell voltage, output,

15 output density, and generating efficiency were measured.

The results are described in Table 3.

[Table 3]

Type	Open circuit voltage (V)	Fuel utilization (%)	Cell voltage (V)	Output (W)	Output density (W/cm ²)	Generating efficiency LHV (%)
Solid electrolyte fuel cell 2 of the aspect of the invention	1.010	80	0.620	76.2	0.645	40

It is confirmed that, even though the solid electrolyte fuel cell 2 ~~of the aspect of the invention~~ of Table 3 and the conventional solid electrolyte fuel cell of Table 2 have the same structure with the exception of the anode, the solid electrolyte fuel cell 2 of the aspect of the invention ~~have the~~ has excellent load current density open circuit voltage, fuel utilization, cell voltage, output, output density, and generating efficiency in comparison with the conventional solid electrolyte fuel cell.

In example 3, the intermediate layer, which is formed in the anode of the power generation cell 2 ~~of the aspect of the invention~~, includes a single layer. However, the intermediate layer may include two or more layers and the layers may be layered so that the nickel content is continuously or intermittently increased in the direction from the innermost layer to the outermost layer, thereby producing the anode. Furthermore, the intermediate layer

may include more layers to form the anode having a nickel composition gradient where the nickel content is increased in the direction from the innermost surface to the outermost surface in a thickness direction as disclosed in (1).